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(54) **Rubber containing starch reinforcement and tire having component thereof**

(57) The present invention relates to a rubber composition containing a combination of starch, modified starch and/or starch/plasticizer composite together with selected methylene donor and/or methylene acceptor compounds. The invention also relates to tires having at least one component comprised of such rubber composition. Such tire component can be, for example, its circumferential tread.

DescriptionField

- 5 **[0001]** The present invention relates to a rubber composition containing a combination of starch, modified starch and/or starch/plasticizer composite together with selected methylene donor and/or methylene acceptor compounds. The invention also relates to tires having at least one component comprised of such rubber composition. Such tire component can be, for example, its circumferential tread or other component of the tire.

10 Background

[0002] Starch, modified starch and starch/plasticizer composites have sometimes been used in various compositions which might have included elastomer formulations, for various purposes which might have included tire components such as tire treads.

- 15 **[0003]** Such materials might be used alone or in conjunction with silica and/or carbon black reinforcing fillers or also with other fillers such as, for example, recycled, or ground, vulcanized rubber particles, short fibers, kaolin clay, mica, talc, titanium oxide and limestone. Such short fibers can be, for example, fibers of cellulose, aramid, nylon, polyester and carbon composition.

[0004] US-A- 5,403,923, 5,258,430, and 4,900,361 disclose the preparation and use of various starch compositions and US-A- 5,672,639 relates to use of starch/plasticizer composites in rubber compositions including as a tire component such as a tire tread.

[0005] However, use of starch-based fillers, in general, may present some limitations as reinforcement for various elastomers where resistance to abrasion and tear properties for elastomer composition are significantly desirable properties.

- 25 **[0006]** Accordingly, it is desired to enhance the use of starch-based materials in elastomer compositions.

[0007] Historically, starch may typically be represented as a carbohydrate polymer having repeating units of amylose (anhydroglucopyranose units joined by glucosidic bonds) and amylopectin, a branched chain structure, as is well known to those having skill in such art. Often, starch is composed of 25 percent amylose and 75 percent amylopectin. [The Condensed Chemical Dictionary, Ninth Edition (1977, revised by G.G. Hawley, published by Van Nostrand Reinhold Company, page 813]. Starch can be, reportedly, a reserve polysaccharide in plants such as, for example, corn, potatoes, rice and wheat as typical commercial sources.

[0008] Starch by itself typically has a softening point of 200°C or above and, therefore, usually is thought of as having a somewhat limited use in many rubber products, primarily because rubber compositions are normally processed by preliminarily blending rubber with various ingredients at temperatures in a range of 140°C to 170°C, usually at least 160°C, and sometimes up to 180°C which is not a high enough temperature to cause the starch (with softening temperature of at least 200°C) to effectively melt and efficiently blend with the rubber composition. As a result, the starch particles tend to remain in individual domains, or granules, within the rubber composition rather than as a more homogeneous blend.

[0009] Accordingly, starch is sometimes modified with a plasticizer of lower softening point to create a starch/plasticizer composite for use in rubber compositions.

[0010] The term "phr" as used herein, and according to conventional practice, refers to "parts of a respective material per 100 parts by weight of rubber, or elastomer".

[0011] In the description of this invention, the terms "rubber" and "elastomer" where used herein, may be used interchangeably, unless otherwise prescribed. The terms "rubber composition", "compounded rubber" and "rubber compound", where used herein, are used interchangeably to refer to "rubber which has been blended or mixed with various ingredients and materials" and such terms are well known to those having skill in the rubber mixing or rubber compounding art.

[0012] The term "carbon black" as used herein means "carbon blacks having properties typically used in the reinforcement of elastomers, particularly sulfur curable elastomers".

50 **[0013]** The term "silica" as used herein can relate to precipitated or fumed silica and typically relates to precipitated silica, including an aluminosilicate, which is well known to those having skill in such art.

[0014] A reference to an elastomer's Tg refers to its glass transition temperature, which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10°C per minute.

55 Summary and Practice of the Invention

[0015] In accordance with one aspect of this invention, a rubber composition is provided which comprises (A) 100 parts by weight of at least one diene-based elastomer, (B) 0.1 to 120, alternatively 25 to 90, phr of at least one elas-

5 tomer reinforcing filler composed of (1) 0.1 to 120, alternatively 5 to 70, phr of at least one starch-based material selected from at least one of starch, starch/plasticizer composite and modified starch, and (2) zero to 90, alternatively 20 to 85, phr of (a) carbon black or silica, namely an amorphous silica or (b) carbon black and silica, namely an amorphous silica; and, optionally, at least one additional inorganic reinforcing or non-reinforcing filler, (C) optionally a coupler for said starch-based material and silica, if silica is used, where said coupler has a moiety reactive with the surface of said starch composite and the surface of said silica, as the case may be, and a moiety interactive with the said elastomer, and (D) a methylene acceptor and/or methylene donor exclusive of hexamethylene tetramine.

[0016] Preferably, said modified starch is selected from at least one of hydroxyethylated starch, oxidized starch and acid modified starch.

10 **[0017]** In practice, said starch is typically composed of amylose units and amylopectin units in a ratio of 15/85 to 35/65, alternatively 20/80 to 30/70, and has a softening point according to ASTM No. D1228 in a range of 180°C to 220°C; and the starch/plasticizer has a softening point in a range of 110°C to 170°C according to ASTM No. D1228

[0018] In the practice of this invention it is preferred that the methylene donor compound contains an -CH₂OX group wherein X is an alkyl radical having from one to 8 carbon atoms, preferably selected from methyl, ethyl, propyl and octyl radicals and is exclusive of hexamethylene tetramine, for example, see US-A- 5,886,074.

15 **[0019]** Representative of such methylene donor compounds, exclusive of hexamethylene tetramine are, for example, hexamethoxymethylmelamine, hexaethoxymethylmelamine and ethoxymethylpyridinium chloride; and N-methylol derivatives of melamine such as, for example N,N',N''-trimethylolmelamine, N-methylolmelamine and N',N''-dimethylolmelamine.

20 **[0020]** Representative of methylene acceptor compounds are, for example, phenolic cashew nut oil resins, resorcinol monobenzoate and polyhydric phenoxy resin, preferably phenolic cashew nut oil resin, for example, see US-A- 5,206,289 and 4,605,696.

[0021] Such phenolic cashew nut oil resins may be available, for example, as SP6700 from the Schnectady company.

25 **[0022]** Phenolic resins are conventionally produced by an acid condensation of phenol, or a mixture of phenols, with an aldehyde, usually formaldehyde. Such phenolic resins might be referred to as two-stage resins and are conventionally known as novolacs. This technology is understood to be well known to those having skill in such art. The Schenectady resin SP6700 is a two-stage phenolic resin from a condensation of a phenol and aldehyde, (a novolac), in which the phenolic component is a mixture of phenol and liquid cashew nut oil which might sometimes be referred to as "CSL". The CSL might be described as a mixture of primarily monophenols substituted in the meta position with C15 hydrocarbon chains.

30 **[0023]** A significant feature of this invention is that it has been observed that hexamethylene tetramine, a well known methylene donor, did not work satisfactorily for use in this invention where the starch-based materials are utilized either by itself or in combination with the preferred methylene acceptors, namely, phenolic cashew nut oil resins. This result was unexpected and illustrated that not all methylene donor compounds, as a chemical class of materials, work satisfactorily for the purposes of this invention.

[0024] A significant aspect of use of a methylene donor, exclusive of hexamethylene tetramine, in combination with starch, modified starch or starch/plasticizer composite is an observed improvement in tear resistance of a rubber composition which is an important physical property of rubber compositions to be used for various components of a tire.

40 **[0025]** In practice, it has been observed herein that the hexamethylene tetramine, which is often thought of as being a methylene donor (see US-A- 5,886,074) was not observed herein to behave in a manner similar to other common methylene donors such as for example hexamethoxymethylmelamine.

[0026] A significant aspect is that it has been observed herein that the use of a methylene donor or a methylene acceptor, or a combination of both, resulted in an improved tear resistance property for a vulcanized rubber composition.

45 **[0027]** In particular, it has been observed herein that a significant aspect of use of a combination of methylene acceptor, particularly a phenolic cashew nut oil resin, and methylene donor, exclusive of hexamethylene tetramine, in combination with starch, modified starch or starch/plasticizer composite provided an improved tear resistance property for a vulcanized rubber composition better than use of a silane coupling agent alone for tear resistance improvement.

50 **[0028]** In practice, the moiety of the coupling agent which is reactive with the starch, modified starch and starch/plasticizer composite as well as silica surfaces is generally considered herein as being capable of reacting with at least one or more hydroxyl groups on their surfaces and possibly with other reactive groups thereon.

[0029] In the practice of this invention, the starch, modified starch and starch/plasticizer composite may be desired to be used, for example, as a free flowing, dry powder or in a free flowing, dry pelletized form.

55 **[0030]** With regard to the modified starch, various modified starches may be utilized. Representative of commercially available modified starches are, for example hydroxyethylated starch as ETHYLEX 2095, oxidized starch as STACOTE H44 and acid modified starch as ECLIPSE G, all from the A.E. Staley Manufacturing Company.

[0031] Where the modified starch is a hydroxyethylated starch, it might be described, for example, as a starch which

has been subjected to a treatment in which hydroxyethyl groups have been substituted for a very small number of hydroxyl groups of the starch.

[0032] With regard to the starch/plasticizer composite, it is desired that the synthetic plasticizer itself is compatible with the starch, and has a softening point lower than the softening point of the starch so that it causes the softening of the blend of the plasticizer and the starch to be lower than that of the starch alone. This phenomenon of blends of compatible polymers of differing softening points having a softening point lower than the highest softening point of the individual polymer(s) in the blend is well known to those having skill in such art.

[0033] For the purposes of this invention, the plasticizer effect for the starch/plasticizer composite, (meaning a softening point of the composite being lower than the softening point of the starch), can be obtained through use of a polymeric plasticizer such as, for example, poly(ethylenevinyl alcohol) with a softening point of less than 160°C. Other plasticizers, and their mixtures, are contemplated for use in this invention, provided that they have softening points of less than the softening point of the starch, and preferably less than 160°C, which might be, for example, one or more copolymers and hydrolyzed copolymers thereof selected from ethylene-vinyl acetate copolymers having a vinyl acetate molar content of from 5 to 90, alternatively 20 to 70, percent, ethylene-glycidyl acrylate copolymers and ethylene-maleic anhydride copolymers. As hereinbefore stated hydrolyzed forms of copolymers are also contemplated. For example, the corresponding ethylene-vinyl alcohol copolymers, and ethylene-acetate vinyl alcohol terpolymers may be contemplated so long as they have a softening point lower than that of the starch and preferably lower than 160°C.

[0034] In general, for the starch/plasticizer composite, the blending of the starch and plasticizer involves what are considered or believed herein to be relatively strong chemical and/or physical interactions between the starch and the plasticizer.

[0035] In general, the starch/plasticizer composite has a desired starch to plasticizer weight ratio in a range of 0.5/1 to 4/1, alternatively 1/1 to 2/1, so long as the starch/plasticizer composition has the required softening point range, and preferably, is capable of being a free flowing, dry powder or extruded pellets, before it is mixed with the elastomer(s).

[0036] While, for the starch/plasticizer composite, the synthetic plasticizer(s) may have a viscous nature at room temperature, or at 23°C and, thus, considered to be a liquid for the purposes of this description, although the plasticizer may actually be a viscous liquid at room temperature since it is to be appreciated that many plasticizers are polymeric in nature.

[0037] For the starch/plasticizer composite, representative examples of synthetic plasticizers are, for example, poly(ethylenevinyl alcohol), cellulose acetate and diesters of dibasic organic acids, so long as they have a softening point sufficiently below the softening point of the starch with which they are being combined so that the starch/plasticizer composite has the required softening point range.

[0038] Preferably, the synthetic plasticizer is selected from at least one of poly(ethylenevinyl alcohol) and cellulose acetate.

[0039] For example, for the starch/plasticizer composite, the aforesaid poly(ethylenevinyl alcohol) might be prepared by polymerizing vinyl acetate to form a poly(vinylacetate) which is then hydrolyzed (acid or base catalyzed) to form the poly(ethylenevinyl alcohol). Such reaction of vinyl acetate and hydrolyzing of the resulting product is well known to those skilled in such art.

[0040] For example, vinylalcohol/ethylene (60/40 mole ratio) copolymers can be obtained in powder forms at different molecular weights and crystallinities such as, for example, a molecular weight of 11700 with an average particle size of 11.5 microns or a molecular weight (weight average) of 60,000 with an average particle diameter of less than 50 microns.

[0041] For the starch/plasticizer composite, various blends of starch and ethylenevinyl alcohol copolymers can then be prepared according to mixing procedures well known to those having skill in such art. For example, a procedure might be utilized according to a recitation in the publication by Bastioli, Bellotti and Del Trediu entitled "A Polymer Composition Including Destructured Starch An Ethylene Copolymer", US-A- 5,403,374.

[0042] Other plasticizers might be prepared, for example and so long as they have the appropriate Tg and starch compatibility requirements, by reacting one or more appropriate organic dibasic acids with aliphatic or aromatic diol(s) in a reaction which might sometimes be referred to as an esterification condensation reaction. Such esterification reactions are well known to those skilled in such art.

[0043] In the practice of this invention, the aforesaid additional inorganic fillers may be, for example, selected from one or more of kaolin clay, talc, short discrete fibers, thermoplastic powders such as polyethylene and polypropylene particles, or other reinforcing or non-reinforcing inorganic fillers.

[0044] In the description of this invention, such additional inorganic fillers are intended to be exclusive of, or to not include, pigments conventionally used in the compounding, or preparation of, rubber compositions such as zinc oxide, titanium oxide and the like, although, of course zinc oxide is conventionally used in the rubber compositions of this invention.

[0045] The additional short fibers for use in the rubber composition of this invention may be, for example, of organic polymeric materials such as cellulose, aramid, nylon and polyester.

[0046] In practice, the said starch/synthetic plasticizer composite has a moisture content in a range of zero to 30, alternatively one to six, weight percent.

[0047] In practice, as hereinbefore pointed out, the elastomer reinforcement may be (i) the starch/plasticizer composite or (ii) a combination of the starch/plasticizer composite and at least one of carbon black and amorphous silica, particularly precipitated silica or (iii) optionally a combination of the starch/plasticizer, carbon black and/or precipitated silica and at least one other inorganic filler, wherein a coupler is optionally used to couple the starch composite and the silica, if silica is used, to the diene based elastomer(s).

[0048] It is considered herein that, where desired, the said starch-based material can be used as (i) a partial or (ii) complete replacement for carbon black and/or silica reinforcement for sulfur vulcanizable elastomers, depending somewhat upon the properties desired for the cured, or vulcanized, rubber composition.

[0049] In practice, it is generally preferred that the rubber reinforcing carbon black is used in conjunction with the said starch-based material in an amount of at least 5 and preferably at least 35 phr of carbon black, depending somewhat upon the structure of the carbon black. Carbon black structure is often represented by its DBP (dibutylphthalate) value. Reinforcing carbon blacks typically have a DBP number in a range of 40 to 400 cc/100 gm, and more usually in a range of 80 to 300 (ASTM D 1265). If the carbon black content is used with a view to providing an elastomer composition with a suitable electrical conductivity to retard or prevent appreciable static electricity build up, a minimum amount of carbon black in the elastomer composition might be, for example, 10 phr of a highly electrically conductive carbon black is used, otherwise usually at least 25 and often at least 35 phr of carbon black is used.

[0050] If desired, and on a practical basis, it is usually preferred that the coupling agent for the said starch-based material can be the same coupler as could be used for the silica, if silica is used. Thus, it is considered herein that the moiety of the coupling agent reactive with the surface of the starch-based material is also reactive with the hydroxyl (e.g. SiOH) groups, and/or other reactive groups, typically on the surface of the silica.

[0051] It is important to appreciate that, preferably, the said starch-based material is not used as a total replacement for carbon black and/or silica in an elastomer composition. Thus, in one aspect, it is considered that the starch-based material is to be typically used as a partial replacement for carbon black and/or silica reinforcement for sulfur vulcanizable elastomers.

[0052] It is important to appreciate that, while starch itself might be used in combination with the starch/plasticizer composite, they are not considered herein as equal alternatives. Thus, while starch might sometimes be considered suitable as a reinforcement for the elastomer composition together with the coupling agent, the starch/plasticizer composite may be considered more desirable for some applications, even when used without a coupling agent.

[0053] If silica is used as a reinforcement together with carbon black, the weight ratio of silica to carbon black is desirably in a weight ratio in a range of 0.1/1 to 10/1, thus at least 0.1/1, alternatively at least 0.9/1, optionally at least 3/1 and sometimes at least 10/1.

[0054] The weight ratio of said silica coupler to the starch composite and silica, if silica is used, may, for example, be in a range of 0.01/1 to 0.2/1 or even up to 0.4/1.

[0055] The starch is recited as being composed of amylose units and/or amylopectin units. These are well known components of starch. Typically, the starch is composed of a combination of the amylose and amylopectin units in a ratio of 25/75. A somewhat broader range of ratios of amylose to amylopectin units is recited herein in order to provide a starch for the starch composite which interact with the plasticizer somewhat differently. For example, it is considered herein that suitable ratios may be from 20/80 up to 100/0, although a more suitable range is considered to be 15/85 to 35/65. Thus, the starch may be composed primarily or even entirely of amylose units.

[0056] The starch can typically be obtained from naturally occurring plants, as hereinbefore referenced. Corn starch is believed to be a rather common natural starch. The starch/plasticizer composite can be present in various particulate forms such as, for example, fibrils, spheres or macromolecules, which may, in one aspect, depend somewhat upon the ratio of amylose to amylopectin in the starch as well as the plasticizer content in the composite.

[0057] The relative importance, if any, of such forms of the starch is the difference in their reinforcing associated with the filler morphology. The morphology of the filler primarily determines the final shape of the starch composite within the elastomer composition, in addition, the severity of the mixing conditions such as high shear and elevated temperature can allow to optimize the final filler morphology. Thus, the starch composite, after mixing, may be in a shape of one or more of hereinbefore described forms.

[0058] It is important to appreciate that the starch, by itself, is hydrophilic in nature, meaning that it has a strong tendency to bind or absorb water. Thus, the moisture content for the starch and/or starch composite has been previously discussed herein. This is considered to be an important, or desirable, feature in the practice of this invention because water can also act somewhat as a plasticizer with the starch and which can sometimes associate with the plasticizer itself for the starch composite such as polyvinyl alcohol and cellulose acetate, or other plasticizer which contain similar functionalities such as esters of polyvinyl alcohol and/or cellulose acetate or any plasticizer which can depress the melting point of the starch.

[0059] Various grades of the starch/plasticizer composition can be developed to be used with various elastomer

compositions and processing conditions.

[0060] As hereinbefore pointed out, the starch typically has a softening point in a range of 180°C to 220°C, depending somewhat upon its ratio of amylose to amylopectin units, as well as other factors and, thus, does not readily soften when the rubber is conventionally mixed, for example, at a temperature in a range of 140°C to 165°C. Accordingly, after
5 the rubber is mixed, the starch remains in a solid particulate form, although it may become somewhat elongated under the higher shear forces generated while the rubber is being mixed with its compounding ingredients. Thus, the starch remains largely incompatible with the rubber and is typically present in the rubber composition in individual domains.

[0061] However, it is now considered herein that providing starch in a form of a starch composite of starch and a plasticizer is particularly beneficial in providing such a composite with a softening point in a range of 110°C to 160°C.

[0062] The plasticizers can typically be combined with the starch such as, for example, by appropriate physical mixing processes, particularly mixing processes that provide adequate shear force.

[0063] The combination of starch and, for example, polyvinyl alcohol or cellulose acetate, is referred to herein as a "composite". Although the exact mechanism may not be completely understood, it is believed that the combination is not a simple mixture but is a result of chemical and/or physical interactions. It is believed that the interactions lead to a
15 configuration where the starch molecules interact via the amylose with the vinyl alcohol, for example, of the plasticizer molecule to form complexes, involving perhaps chain entanglements. The large individual amylose molecules are believed to be interconnected at several points per molecule with the individual amylopectin molecules as a result of hydrogen bonding (which might otherwise also be in the nature of hydrophilic interactions).

[0064] This is considered herein to be beneficial because by varying the content and/or ratios of natural and synthetic components of the starch/plasticizer composite it is believed to be possible to alter the balance between hydrophobic and hydrophilic interactions between the starch components and the plasticizer to allow, for example, the starch composite filler to vary in form from spherical particles to fibrils.

[0065] In particular, it is considered herein that adding a polyvinyl alcohol to the starch to form a composite thereof, particularly when the polyvinyl alcohol has a softening point in a range of 90°C to 130°C, can be beneficial to provide
25 resulting starch/plasticizer composite having a softening point in a range of 110°C to 160°C, and thereby provide a starch composite for blending well with a rubber composition during its mixing stage at a temperature, for example, in a range of 110°C to 165°C or 170°C.

[0066] In a further aspect of the invention, a tire is provided having at least one component comprised of the said starch-based material containing rubber composition of this invention. Although not limited thereto, such tire components can be at least one of tread, tread base or tread undertread, tire innerliner, sidewall apexes, wedges for the tire
30 shoulder, sidewall, carcass ply and breaker wire coating rubber compositions, bead insulation rubber composition and cushion or gumstrips for addition to various parts of the tire construction. As used herein, the tread and tread base may be collectively referred to herein as the "tread", or "circumferential tread". Such tire components are well known those skilled in such art.

[0067] As an aspect feature of this invention, a tire is provided having a circumferential tread component comprised of the said rubber composition of this invention with the aforesaid tire component, thus, being its tread. As is well known to those skilled in such art, such tire tread is typically designed to be ground-contacting.

[0068] As a further aspect of this invention, a tire is provided with sidewall apex components comprised of the said rubber composition of this invention.

[0069] As an additional aspect of the invention, a tire is provided with a sidewall insert component positioned in the tire sidewall and apart from its bead portion comprised of the rubber composition of this invention where it might be desired to modify the physical properties of the tire sidewall.

[0070] Historically, the more homogeneous the dispersion of rubber compound components into the rubber, the better the resultant cured properties of that rubber. It is considered herein that it is a particular feature of this invention
45 that the starch composite mixes with the rubber composition during the rubber mixing under high shear conditions and at a temperature in a range of 140°C to 165°C, in a manner that very good dispersion in the rubber mixture is obtained. This is considered herein to be important because upon mixing the elastomer composition containing the starch/plasticizer composite to a temperature to reach the melting point temperature of the composite, the starch composite will contribute to the development of high shearing forces which is considered to be beneficial to ingredient dispersion within the rubber composition. Above the melting point of the starch composite, for example, around 150°C, it will melt and maximize its reaction with the coupling agent.

[0071] In one aspect, such a rubber composition can be provided as being sulfur cured. The sulfur curing is accomplished in a conventional manner, namely, by curing under conditions of elevated temperature and pressure for a suitable period of time.

[0072] In the practice of this invention, as hereinbefore pointed out, the rubber composition is comprised of at least one diene-based elastomer, or rubber. Thus, it is considered that the elastomer is a sulfur curable elastomer. The diene-based elastomer may be selected from at least one of homopolymers of isoprene and 1,3-butadiene and copolymers of isoprene and/or 1,3-butadiene with an aromatic vinyl compound selected from at least one of styrene and alpha-meth-
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ylstyrene. Accordingly such elastomer, or rubber, may be selected, for example, from at least one of cis 1,4-polyisoprene rubber (natural and/or synthetic, and preferably natural rubber), 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, isoprene/butadiene copolymer rubbers, styrene/isoprene copolymer rubbers, styrene/isoprene/butadiene terpolymer rubbers, cis 1,4-polybutadiene rubber and medium to high vinyl polybutadiene rubber having a vinyl 1,2- content in a range of 15 to 85 percent and emulsion polymerization prepared butadiene/acrylonitrile copolymers. Such medium to high vinyl polybutadiene rubber may be more simply referred to herein as a high vinyl polybutadiene.

[0073] The rubber composition is preferably of at least two diene-based rubbers.

[0074] In one aspect, an emulsion polymerization derived styrene/butadiene (E-SBR) might be used having a relatively conventional styrene content of 20 to 30 percent bound styrene or, for some applications, an E-SBR having a medium to relatively high bound styrene content, namely, a bound styrene content of 30 to 45 percent.

[0075] The relatively high styrene content of 30 to 45 for the E-SBR can be considered beneficial for a purpose of enhancing traction, or skid resistance, of the tire tread. The presence of the E-SBR itself is considered beneficial for a purpose of enhancing processability of the uncured elastomer composition mixture, especially in comparison to a utilization of a solution polymerization prepared SBR (S-SBR).

[0076] By emulsion polymerization prepared E-SBR, it is meant that styrene and 1,3-butadiene are copolymerized as an aqueous emulsion. Such are well known to those skilled in such art. The bound styrene content can vary, for example, from 5 to 50%.

[0077] Emulsion polymerization prepared styrene/butadiene/acrylonitrile copolymer rubbers (E-SBAR) containing 2 to 50 weight percent bound acrylonitrile in the terpolymer are also contemplated as diene-based rubbers for use in this invention.

[0078] The solution polymerization prepared SBR (S-SBR) typically has a bound styrene content in a range of 5 to 50, preferably 9 to 36, percent. Its' butadiene portion may have a vinyl content in a range of 10 to 50 percent. The S-SBR can be conveniently prepared, for example, by organo lithium catalyzation in the presence of an organic hydrocarbon solvent.

[0079] A purpose of using S-SBR is to enhance tire rolling resistance since it should tend to promote lower hysteresis for tire tread compositions.

[0080] The 3,4-polyisoprene rubber (3,4-PI) is considered beneficial for a purpose of enhancing the tire's traction when it is used in a tire tread composition.

[0081] The 3,4-PI and use thereof is more fully described in US-A- 5,087,668. The T_g refers to the glass transition temperature which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10°C per minute.

[0082] The cis 1,4-polybutadiene rubber (BR) is considered to be beneficial for a purpose of enhancing the tire tread's wear, or treadwear.

[0083] Such BR can be prepared, for example, by organic solution polymerization of 1,3-butadiene.

[0084] The BR may be conveniently characterized, for example, by having at least a 90% cis 1,4-content.

[0085] The cis 1,4-polyisoprene and cis 1,4-polyisoprene natural rubber are well known to those having skill in the rubber art.

[0086] The commonly-employed siliceous pigments used in rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica), although precipitate silicas are preferred.

[0087] Amorphous silicas preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate. Such precipitated silicas are intended to include aluminosilicates.

[0088] Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of 40 to 600, and more usually in a range of 50 to 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, page 304 (1930).

[0089] The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of 50 to 400 cm³/100g, and more usually 100 to 300 cm³/100g.

[0090] Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc, with, for example, Zeosil 1165MP and silicas available from Degussa AG with, for example, designations VN2 and VN3, as well as other grades of silica, particularly precipitated silicas, which can be used for elastomer reinforcement.

[0091] The amorphous silicas are conventionally used in conjunction with a coupling agent and it is intended herein that the coupling agent may be also be reactive with starch-based materials used for this invention, particularly with hydroxyl groups of the starch based materials.

[0092] While various coupling agents may be used, a variety of coupling agents is a coupling agent is comprised of a bis (3-trialkoxysilylalkyl) polysulfide wherein said alkyl groups for the trialkoxy component are selected from methyl and ethyl radicals, wherein said alkyl group for said silylalkyl component is selected from ethyl, propyl and butyl radicals and wherein the polysulfide bridge contains an average of 2.2 to 4 connecting sulfur atoms.

[0093] Exemplary of such coupling agent is a bis-(3-triethoxysilylpropyl) polysulfide where the polysulfide bridge contains an average of from 2.2 to 4 and particularly an average of from 2.2 to 2.6, (a disulfide material), or an average of from 3.4 to 4, (a tetrasulfide material), 4 sulfur atoms in its polysulfide bridge.

[0094] It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

[0095] Typical amounts of tackifier resins, if used, comprise 0.5 to 10 phr, usually 1 to 5 phr. Typical amounts of processing aids comprise 1 to 50 phr. Such processing aids can include, for example, aromatic, naphthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise 1 to 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in The Vanderbilt Rubber Handbook (1978), pages 344-346. Typical amounts of antiozonants comprise 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise 0.5 to 3 phr. Typical amounts of zinc oxide comprise 1 to 10 phr. Typical amounts of waxes comprise 1 to 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise 0.1 to 1 phr.

[0096] The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from 0.5 to 4 phr, or even, in some circumstances, up to 8 phr.

[0097] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from 0.5 to 4, preferably 0.8 to 1.5, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts (of 0.05 to 3 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

[0098] The presence and relative amounts of the above additives are not considered to be an aspect of the present invention which is more primarily directed to the utilization of specified blends of rubbers in rubber compositions, in combination with various starch, modified starch and starch/plasticizer composite and methylene donor and/or methylene acceptor compounds in various rubber compositions.

[0099] The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely, at least one non-productive stage followed by a productive mix stage. The final curatives are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, starch-based material, and fillers such as carbon black and optional silica and coupler, and/or non-carbon black and non-silica fillers, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

[0100] The rubber composition of this invention can be used for various purposes. For example, it can be used for various tire compounds. Such tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art.

[0101] The invention may be better understood by reference to the following examples in which the parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

[0102] In this Example, three fillers are utilized in a natural rubber composition.

[0103] The three fillers are carbon black, silica and starch-based material wherein the starch-based material is utilized as corn starch or as a starch/plasticizer composite.

[0104] The basic formulation is shown in Table 1 in which the silica, starch or starch/plasticizer composite, as well as the coupling agent are shown as being used in variable amounts.

[0105] In Table 2 the variable amounts of the silica, starch or starch/plasticizer composite and coupling agent are shown as well as various physical properties of the resulting rubber composition.

[0106] The individual rubber samples are shown in Tables 2 and 2A as Samples A-F, wherein all of the Samples contained silica and a coupling agent, Samples C and D also contained starch and Samples E and F also contained a starch/plasticizer composite.

[0107] The rubber compositions containing the materials illustrated in Table 1 were prepared in a Kobe Banbury rubber mixer using three separate, sequential stages of addition (mixing), namely, two non-productive mix stages, in which ingredients are added during both non-productive mixing stages and one final productive mix to temperatures of 160°C, 150°C, and 108°C, respectively, and times of 4 minutes, 4 minutes and 2 minutes, respectively. However, the silica and coupler are added in the second non-productive mix stage with the starch compound.

Table 1

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber ¹	100
Carbon black ²	15
Silica ³	Variable (0 or 20)
Starch ⁴	Variable (0 or 20)
Starch composite ⁵	Variable (0 or 20)
Coupling agent ⁶	Variable (0 or 3)
Processing oil ⁷	5
Zinc oxide	5
Antioxidant ⁸	2
Fatty acid ⁹	2
2nd Non-Productive	
Silica ³	15
Coupling agent ⁶	2
Productive	
Sulfur	1.5
Accelerators ⁹	2.5

1. Synthetic cis 1,4-polyisoprene rubber as NAT2200 from The Goodyear Tire & Rubber Company.

2. N299, a carbon black ASTM designation.

3. HiSil 210 from PPG Industries, Inc.

4. Mater Bi 1128RR-H from the Novamont company as a composite of starch and ethylene vinyl copolymer (40/50 weight ratio) with natural plasticizers, having a softening point of 147°C.

5. Unmodified corn starch as Staley Pearl Starch, a trademark of the A.E. Staley Manufacturing Company.

6. A coupler as a 50% active composite composed of an organosilane tetrasulfide on or with carbon black in a 50/50 weight ratio available as material X50S from Degussa AG. Technically the organosilane polysulfide is understood to be a composite, or mixture, in which the average polysulfide bridge contains 3.5 to 4 connecting sulfur atoms, although the mixture may contain such polysulfides with 2 to 8 connecting sulfur atoms.

7. Flexon 641 from Exxon.

8. Of the quinoline type.

9. A combination of sulfenamide with a minor amount of diphenylguanidine.

[0108] The resulting Samples are vulcanized for 36 minutes at a temperature of 150°C. and various of their physical properties are shown in the following Tables 2 and 2A.

Table 2

Ingredients	Sample A	Sample B	Sample C
Carbon black	15	15	15
Silica	35	35	15
Starch	0	0	20
Starch composite	0	0	0
Coupling agent	2	5	2
Properties			
A. Rheometer (150°C)			
Max. Torque, dNm	41.5	44.6	41.3
Min. Torque, dNm	6.8	6.2	6.1
Delta torque, dNm	34.7	38.4	34.8
T ₉₀ , minutes	17.4	15.7	12.7
B. Stress-Strain			
Tensile strength, MPa	24.4	25.9	18.9
Elongation @ break, %	561	527	490
Modulus, 300%, MPa	9.1	11.8	7.6
C. Rebound, 100°C, %	66	68	80
D. Hardness, Shore A, 23°C	62	65	58
E. Tear strength, N, 95°C	142	73	18
F. DIN abrasion	145	133	208

Table 2A

(a Continuation of Table 2)			
Ingredients	Sample D	Sample E	Sample F
Carbon black	15	15	15
Silica	15	15	15
Starch	20	0	0
Starch composite	0	20	20
Coupling agent	5	2	5
Properties			
A. Rheometer (150°C)			
Max Torque, dNm	46	38.9	40.1
Min Torque, dNm	5.8	5.9	5.5
Delta torque, dNm	40.2	33	34.6
T ₉₀ , minutes	15.8	12.7	13.2
B. Stress-Strain			
Tensile strength, MPa	19.2	20	20.1
Elongation at break,	448	485	438
Modulus, 300%, MPa	9.7	10.0	12.6
C. Rebound, 100°C, %	78	76	76
D. Hardness, Shore A, 23°C	63	63	65
E. Tear strength, N, 95°C	14	15	14
F. DIN abrasion	204	196	186

[0109] The tensile strength values are measures of maximum stress when the sample specimen reaches its maximum elongation. Such physical property is well known to those having skill in such art.

[0110] The elongation values are measures of maximum elongation of the sample specimen before failure. Such physical property is well known those having skill in such art.

[0111] The Shore A hardness values are measures of a sample's resistance to localized plastic deformation.

[0112] The Rebound values are measures of a sample's capacity to adsorb energy when it is deformed under load and recovers upon removing the applied load.

[0113] The DIN abrasion values are measures of relative volume loss of a sample upon exposure to an applied abrasive wheel under specified load as compared to a comparative control rubber composition. Lower values are indicative of greater resistance to abrasion. The DIN test is conducted at a load of 2 Kg.

[0114] It is readily seen from Tables 2 and 2A that use of a reduced amount of silica in combination with corn starch (Samples C and D) or with a starch/plasticizer composite (Samples E and F) resulted in improved Rebound, with a significant loss of tear strength and abrasion resistance when compared to Samples A and B.

[0115] It is also readily seen that the DIN abrasion resistance of the rubber compositions which used the starch/plasticizer composite (Samples E and F) were better than the corn starch-containing rubber composition of Samples C and D.

[0116] Therefore, it is concluded herein, as observed, that the replacement of silica with corn starch in a carbon black/silica reinforced rubber composition provides higher rebound, but a sharp loss of abrasion resistance and tear resistance. The starch/plasticizer composite is observed to be better for abrasion resistance than the unmodified corn starch.

EXAMPLE II

[0117] Additional rubber samples are prepared using the rubber composition shown in the following Table 3 using a procedure described in Example I except that two fillers are used, namely carbon black and either silica, corn starch or starch/plasticizer composite, instead of three fillers.

[0118] The basic formulation is shown in Table 3 where the silica, corn starch, starch/plasticizer composite and coupling agent are recited as being variable.

[0119] In Table 4 the variable amounts of the silica, starch, starch composite and coupling agent are shown as well as various physical properties of the resulting rubber composition.

[0120] The individual rubber samples are shown in Table 4 as Samples G-L, wherein Samples G and H contained silica, Samples I and J contained corn starch and Samples K and L contained a starch/plasticizer composite.

Table 3

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Antioxidant	2
Fatty acid	2
Zinc oxide	5
2nd Non-Productive	
Silica	Variable (0 or 15)
Starch	Variable (0 or 15)
Starch composite	Variable (0 or 15)
Coupling agent	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0121] The Samples were vulcanized for 36 minutes at 150°C and various physical properties are shown in Tables 4 and 4A.

Table 4

Ingredients	Sample G	Sample H	Sample I
Carbon black	35	35	35
Silica	15	15	0
Starch	0	0	15
Starch composite	0	0	0
Coupling agent	0	2	0
Properties			
A. Rheometer (150°C)			
Max. Torque, dNm	27.6	31.5	34.9
Min. Torque, dNm	6.7	6.2	6
Delta torque, dNm	20.9	25.3	28.9
T ₉₀ , minutes	22.1	19.1	14.7
B. Stress-Strain			
Tensile strength, MPa	21.7	24.2	21.2
Elongation @ break, %	629	593	549
Modulus, 300%, MPa	5.5	8.1	7
C. Rebound, 100°C, %	59	63	72
D. Hardness, Shore A, 23°C	53	56	57
E. Tear strength, N, 95°C	236	240	84
F. DIN abrasion	256	152	208

Table 4A

(a Continuation of Table 4)			
Ingredients	Sample J	Sample K	Sample L
Carbon black	35	35	35
Silica	0	0	0
Starch	15	0	0
Starch composite	0	15	15
Coupling agent	2	0	2
Properties			
A. Rheometer (150°C)			
Max. Torque, dNm	35.2	32.1	34.2
Min. Torque, dNm	5.7	6.7	6.4
Delta torque, dNm	29.5	25.4	27.8
T ₉₀ , minutes	14.6	15.1	14.2
B. Stress-Strain			
Tensile strength, MPa	22.1	22.3	23.9
Elongation @ break, %	555	571	554
Modulus, 300%, MPa	7.5	7.9	9.7
C. Rebound, 100°C, %	70	66	65
D. Hardness, Shore A, 23°C	57	60	62
E. Tear strength, N, 95°C	83	104	138
F. DIN abrasion	198	178	161

[0122] It can readily be seen from Tables 4 and 4A that improved Rebound can be seen in Samples I, J, K and L, where a reduced amount of silica is used and either corn starch has been added (Samples C and D) or starch/plasticizer composite has been added (Samples E and F) as compared to Samples A and B.

[0123] However, the addition of the corn starch or the starch/plasticizer composite as replacements for silica in a carbon black reinforced rubber composition is observed to generate lower tear resistance and worse abrasion resistance for the respective rubber compositions.

[0124] The starch/plasticizer composite containing Samples K and L were observed to yield better tear resistance and abrasion resistance than the unmodified corn starch Samples I and J.

[0125] The silica, corn starch and starch/plasticizer composite containing Samples H, J and L, which also utilized a coupling agent, were all observed to show improved tear resistance and abrasion resistance.

EXAMPLE III

[0126] Additional rubber samples are prepared using the rubber composition shown in the following Table 5 using a procedure described in Example I except that two fillers are used in the absence of silica and coupling agent, namely carbon black and corn starch or starch/plasticizer composite.

[0127] Also, for this Example, methylene donors were added in a form of either hexamethoxymethylmelamine or hexamethylene tetramine. Both are well known methylene donors used in various rubber compositions, for example, see US-A- 5,886,074.

[0128] The basic formulation is shown in Table 5 where the starch, starch/plasticizer composite, hexamethoxymethylmelamine, and hexamethylene tetramine are recited as being variable.

[0129] In Table 6 the variable amounts of the starch, starch/plasticizer composite, hexamethoxymethylmelamine, and hexamethylene tetramine are shown as well as various physical properties of the resulting rubber composition.

EP 1 074 582 A1

[0130] The individual rubber samples are shown in Table 6 as Samples M-R, wherein Samples M-O contained the corn starch and Samples P-R contained the starch/plasticizer composite.

[0131] Samples O and R also contained the hexamethoxymethylmelamine which is typically a methylene donor and Samples N and Q contained the hexamethylene tetramine which is also typically a methylene donor.

Table 5

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Starch	Variable (0 or 15)
Starch composite	Variable (0 or 15)
Hexamethoxymethylmelamine	Variable (0 or 2)
Hexamethylene tetramine	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0132] The Samples were vulcanized for 36 minutes at 150°C and various physical properties are shown in the following Tables 6 and 6A.

Table 6

Ingredients	Sample M	Sample N	Sample O
Starch	15	15	15
Starch composite	0	0	0
Hexamethoxymethylmelamine	0	0	2
Hexamethylene tetramine	0	2	0
Properties			
A. Rheometer (150°C)			
Max. Torque, dNm	34.9	37.1	33
Min. Torque, dNm	6	6.3	6.3
Delta torque, dNm	28.9	30.8	26.7
T ₉₀ , minutes	14.7	10.4	13.4
B. Stress-Strain			
Tensile strength, MPa	21.2	18.6	17.7
Elongation @ break, %	549	508	568
Modulus, 300%, MPa	7	7.8	6
C. Rebound, 100°C, %	72	73	67
D. Hardness, Shore A, 23°C	57	56	53
E. Tear strength, N, 95°C	84	39	112
F. DIN abrasion	208	209	217

Table 6A

(a Continuation of Table 6)			
Ingredients	Sample P	Sample Q	Sample R
Starch	0	0	0
Starch composite	15	15	15
Hexamethoxymethylmelamine	0	0	2
Hexamethylene tetramine	0	2	0
Properties			
A. Rheometer (150°C)			
Max. Torque, dNm	32.1	35	32
Min. Torque, dNm	6.7	7	7
Delta torque, dNm	25.4	28	25
T ₉₀ , minutes	15.1	8.9	14
B. Stress-Strain			
Tensile strength, MPa	22.3	19.4	20
Elongation @ break, %	571	523	560
Modulus, 300%, MPa	7.9	8.7	8.5
C. Rebound, 100°C, %	66	67	65
D. Hardness, Shore A, 23°C	60	58	53
E. Tear strength, N, 95°C	104	42	124
F. DIN abrasion	178	186	174

[0133] It can readily be seen from Tables 6 and 6A that the rubber samples containing the hexamethylene tetramine resulted in a significant reduction in tear resistance with the corn starch (Sample N) or starch/plasticizer composite (Sample Q) reinforced Samples.

[0134] Whereas, the hexamethoxymethyl melamine addition resulted in a significant improvement in tear resistance for the corn starch containing rubber sample (Sample O) or rubber sample which contained the starch composite (Sample R) reinforced rubber composition.

[0135] These results illustrate that the choice of methylene donor type of material is critical for the observed tear resistance improvement for the rubber composition containing a starch-based material.

EXAMPLE IV

[0136] Additional rubber samples are prepared using the rubber composition shown in the following Table 7 which is similar to Example III except that a phenolic cashew nut oil resin is also selectively added which is a recognized methylene acceptor.

[0137] The basic formulation is shown in Table 7 where the starch, starch/plasticizer composite, hexamethoxymethylmelamine, hexamethylene tetramine and phenolic cashew nut oil resin are recited as being variable.

[0138] In Tables 8 and 8A the variable amounts of the starch, starch/plasticizer composite, hexamethoxymethylmelamine, hexamethylene tetramine and phenolic cashew nut oil resin are shown as well as various physical properties of the resulting rubber composition.

[0139] The individual rubber samples are shown in Tables 8 and 8A as Samples S-X, wherein Samples S-U contained the corn starch and Samples V-X contained the starch/plasticizer composite.

[0140] Samples U and X also contained the hexamethoxymethylmelamine and Samples T and W contained the hexamethylene tetramine.

[0141] Samples T, U, W and X contained the phenolic cashew nut oil resin.

Table 7

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Starch	Variable (0 or 15)
Starch composite	Variable (0 or 15)
Hexamethoxymethylmelamine	Variable (0 or 2)
Hexamethylene tetramine	Variable (0 or 2)
Phenolic cashew nut oil resin ¹	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

1. Resin as SP6700 from the Schnectady Chemical Company.

[0142] The Samples were vulcanized at a temperature of 150°C for 36 minutes and various physical properties are shown in Tables 8 and 8A.

Table 8

Ingredients	Sample S	Sample T	Sample U
Carbon black	35	35	35
Starch	15	15	15
Starch composite	0	0	0
Hexamethoxymethylmelamine	0	0	2
Hexamethylene tetramine	0	2	0
Phenolic cashew nut oil	0	2	2
Properties			
A. Stress-Strain			
Tensile strength, MPa	21.2	18.3	18.3
Elongation @ break, %	549	511	567
Modulus, 300%, MPa	7	7.8	6.7
B. Rebound, 100°C, %	72	69	64
C. Hardness, Shore A, 23°C	57	60	56
D. Tear strength, N, 95°C	84	58	123
E. DIN abrasion	208	206	213

Table 8A

(a Continuation of Table 8)			
Ingredients	Sample V	Sample W	Sample X
Carbon black	35	35	35
Starch	0	0	0
Starch composite	15	15	15
Hexamethoxymethylmelamine	0	0	2
Hexamethylene tetramine	0	2	0
Phenolic cashew nut oil	0	2	2
Properties			
A. Stress-Strain			
Tensile strength, MPa	22.3	19.9	20.8
Elongation @ break, %	571	523	545
Modulus, 300%, MPa	7.9	9.5	9.5
B. Rebound, 100°C, %	66	64	61
C. Hardness, Shore A, 23°C	60	62	60
D. Tear strength, N, 95°C	104	57	175
E. DIN abrasion	178	188	164

[0143] It can readily be seen from Tables 8 and 8A that rubber compositions containing the combination of hexamethoxymethylmelamine with the phenolic cashew nut oil resin gave improved tear resistance with the corn starch (Sample U) or starch/plasticizer composite (Sample X) and improved abrasion resistance with the starch composite.

[0144] In contrast, rubber compositions containing the combination of hexamethylene tetramine with the phenolic cashew nut oil resin resulted in worse tear resistance with the corn starch or the starch/plasticizer composite (Samples T and W) and no improvement in abrasion resistance with the starch or starch/plasticizer composite (Samples T and W).

[0145] Therefore, it is concluded herein that the hexamethylene tetramine, a typical methylene donor, does not act to provide improved abrasion resistance and tear resistance properties for the rubber composition when used in combination with the phenolic cashew nut oil resin methylene acceptor compound.

EXAMPLE V

[0146] In this Example, various commercially available modified starches are evaluated as fillers in combination with carbon black and compared to unmodified corn starch.

[0147] In particular, an hydroxyethylated starch, an oxidized starch and an acid modified starch are evaluated.

[0148] For some of the rubber compositions, hexamethoxymethylmelamine is also added.

[0149] The preparation procedure of Example I is utilized.

[0150] The rubber samples were prepared using the rubber composition shown in the following Table 9 in which the starch, modified starch(es) and hexamethoxymethylmelamine are shown as being variable.

[0151] In Tables 10 and 10A the variable amounts of the starch, modified starch(es) and hexamethoxymethylmelamine are shown as well as various physical properties of the resulting rubber compositions.

[0152] The individual rubber samples are shown in Tables 10 and 10A as Samples AA-HH, wherein Samples AA and BB contained the corn starch, Samples CC and DD contained the hydroxyethylated starch, Samples EE and FF contained the oxidized starch and Samples GG and HH contained the acid modified starch.

[0153] Samples BB, DD, FF and HH also contained the hexamethoxymethylmelamine.

Table 9

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Starch	Variable (0 or 15)
Starch, modified	Variable (0 or 15)
Hexamethoxymethylmelamine	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0154] The Samples were vulcanized at 150°C for 36 minutes and various physical properties are shown in the following Tables 10 and 10A.

Table 10

Ingredients	AA	BB	CC	DD
Starch	15	15	0	0
Hydroxyethylated starch ¹	0	0	15	15
Oxidized starch ²	0	0	0	0
Acid modified starch ³	0	0	0	0
Hexamethoxymethylmelamine	0	2	0	2
Properties				
A. Rheometer (150°C)				
Max. torque, MPa	14.8	15.1	15	15.1
Min. torque, MPa	1.4	1.7	1.6	1.7
Delta torque	12.6	13.4	13.4	13.4
T ₉₀ , minutes	15	15.9	14.8	15.6
B. Stress-Strain				
Tensile, MPa	19	17.8	18.9	18.1
Elongation (%)	569	561	567	572
Modulus (300%), MPa	6.5	6.5	6.5	6.4
C. Rebound, 100°C, %	68	65	67	65
D. Hardness, Shore A, 100°C	52	53	52	53
E. Tear Strength, N, 95°C	74	111	84	126
F. DIN abrasion	176	181	176	177

1. An hydroxyethylated starch obtained as ETHYLEX 2095 from the A.E. Staley Manufacturing Company.

2. An oxidized starch obtained as STA-COTE H44 from the A.E. Staley Manufacturing Company.

3. An acid modified starch obtained as ECLIPSE G from the A.E. Staley Manufacturing Company.

Table 10A

(a Continuation of Table 10)				
Ingredients	EE	FF	GG	HH
Starch	0	0	0	0
Hydroxyethylated starch ¹	0	0	0	0
Oxidized starch ²	15	15	0	0
Acid modified starch ³	0	0	15	15
Hexamethoxymethylmelamine	0	2	0	2
Properties				
A. Rheometer (150°C)				
Max. torque, MPa	15.2	15.6	15.1	15.3
Min. torque, MPa	1.5	1.7	1.5	1.8
Delta torque	13.7	13.9	13.6	13.5
T ₉₀ , minutes	15.1	15.6	14.8	15.8
B. Stress-Strain				
Tensile, MPa	17.4	16.7	17.2	17.6
Elongation (%)	544	550	539	554
Modulus (300%), MPa	6.5	6.4	6.5	6.6
C. Rebound, 100°C, %	68	65	67	66
D. Hardness, Shore A, 100°C	53	53	52	53
E. Tear Strength, N, 95°C	85	118	73	124
F. DIN abrasion	179	194	184	189

1. An hydroxyethylated starch obtained as ETHYLEX 2095 from the A.E. Staley Manufacturing Company.

2. An oxidized starch obtained as STA-COTE H44 from the A.E. Staley Manufacturing Company.

3. An acid modified starch obtained as ECLIPSE G from the A.E. Staley Manufacturing Company.

[0155] It can readily be seen from Tables 10 and 10A that the rubber compositions containing the hexamethoxymethyl melamine addition (Samples BB, DD, FF and HH) had improved tear resistance as compared to the rubber compositions which contained the unmodified starch (Sample AA) and the modified starch (Samples CC, EE and GG).

EXAMPLE VI

[0156] In this Example, various commercially available modified starches are evaluated as fillers in combination with carbon black as well as the corn starch and as well as a phenolic cashew nut oil resin.

[0157] In particular, use of hydroxyethylated starch, an oxidized starch and an acid modified starch are evaluated.

[0158] For some of the rubber compositions, hexamethoxymethylmelamine and/or phenolic cashew nut oil resin is also added.

[0159] The preparation procedure of Example I is utilized.

[0160] The rubber samples were prepared using the rubber composition shown in the following Table 11 in which the starch, modified starch(es), hexamethoxymethylmelamine and phenolic cashew nut oil resin are shown as being variable.

[0161] In Tables 12 and 12A the variable amounts of the starch, modified starch(es), hexamethoxymethylmelamine and phenolic cashew nut oil resin are shown as well as various physical properties of the resulting rubber compositions.

EP 1 074 582 A1

[0162] The individual rubber samples are shown in Tables 12 and 12A as Samples II-PP, wherein Samples II and JJ contained the corn starch, Samples KK and LL contained the hydroxyethylated starch, Samples MM and NN contained the oxidized starch and Samples OO and PP contained the acid modified starch.

[0163] Samples JJ, LL, NN and PP contained the phenolic cashew nut oil resin as well as the hexamethoxymethylmelamine.

Table 11

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Starch	Variable (0 or 15)
Starch, modified	Variable (0 or 15)
Hexamethoxymethylmelamine	Variable (0 or 2)
Phenolic cashew nut oil resin	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0164] The Samples were vulcanized at 150°C for 36 minutes and various physical properties are shown in the following Tables 12 and 12A.

Table 12

Ingredients	II	JJ	KK	LL
Starch	15	15	0	0
Hydroxyethylated starch	0	0	15	15
Oxidized starch	0	0	0	0
Acid modified starch	0	0	0	0
Hexamethoxymethylmelamine	0	2	0	2
Phenolic cashew nut oil resin	0	2	0	2
Properties				
A. Rheometer (150°C)				
Max. torque, MPa	14.8	15.7	14.5	15.8
Min. torque, MPa	1.5	1.8	1.4	1.7
Delta torque	13.3	13.9	13.1	14.1
T ₉₀ , minutes	15.4	17	14.8	16.9
B. Stress-Strain				
Tensile, MPa	18.8	17.6	18.2	18.3
Elongation (%)	562	540	558	549
Modulus (300%), MPa	6.5	7.1	6.4	7.2
C. Rebound, 100°C, %	70	64	69	65
D. Hardness, Shore A, 100°C	53	54	52	54
E. Tear Strength, N, 95°C	75	92	74	104
F. DIN abrasion	207	211	210	207

Table 12A

(a Continuation of Table 12)				
Ingredients	MM	NN	OO	PP
Starch	0	0	0	0
Hydroxyethylated starch	0	0	0	0
Oxidized starch	15	15	0	0
Acid modified starch	0	0	15	15
Hexamethoxymethylmelamine	0	2	0	2
Phenolic cashew nut oil resin	0	2	0	2
Properties				
A. Rheometer (150°C)				
Max. torque, MPa	14.9	15.7	14.9	15.7
Min. torque, MPa	1.5	1.7	1.5	1.6
Delta torque	13.4	14	13.4	14.1
T ₉₀ , minutes	15.2	17.1	14.9	17.2
B. Stress-Strain				
Tensile, MPa	16.6	16.4	18	17.1
Elongation (%)	536	533	550	530
Modulus (300%), MPa	6.3	6.7	6.5	7.1
C. Rebound, 100°C, %	68	64	69	65
D. Hardness, Shore A, 100°C	52	54	52	54
E. Tear Strength, N, 95°C	80	108	73	95
F. DIN abrasion	210	216	212	210

[0165] It can readily be seen from Tables 12 and 12A that the combination of hexamethoxymethyl melamine and the phenolic cashew nut oil resin resulted in improved tar resistance when used with the unmodified corn oil starch (Sample JJ) or modified starches (Samples LL, NN and PP).

EXAMPLE VII

[0166] In this Example, a starch composite is evaluated as a filler in combination with carbon black. Two control compounds, one containing only carbon black as the filler and the other contains carbon black and silica with a coupling agent. A comparison of the addition of coupling agent, hexamethoxymethylmelamine, or phenolic cashew nut oil resin to the starch/plasticizer composite or the hexamethoxymethylmelamine and phenolic cashew nut oil resin is also included.

[0167] The rubber samples were prepared using the rubber compositions shown in Table 13 in which, for the second non-productive mix stage, the carbon black, silica, coupling agent, starch/plasticizer composite, hexamethoxymethylmelamine and phenolic cashew nut oil resin are shown as being variable. In table 14 and 14A, the variable amounts of the ingredients for the second nonproductive mix stage are shown as well as various cured properties of the resulting rubber compositions.

[0168] The individual rubber samples are shown in Tables 14 and 14A as Samples QQ to WW; wherein all of the samples contained carbon black, and variable amounts of silica, starch/plasticizer composite, coupling agents and methylene donors and acceptors.

Table 13

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Carbon black	Variable (0 or 15)
Silica	Variable (0 or 15)
Coupling agent	Variable (0 or 3)
Starch composite	Variable (0 or 15)
Hexamethoxymethylmelamine	Variable (0 or 2)
Phenolic cashew nut oil resin	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0169] The Samples were vulcanized at 150°C for 36 minutes and various physical properties are shown in Tables 14 and 14A.

Table 14

Ingredients	QQ	RR	SS	TT
Carbon black	50	35	35	35
Silica	0	15	0	0
Coupling agent	0	3	0	3
Starch composite	0	0	15	15
Hexamethoxymethylmelamine	0	0	0	0
Phenolic cashew nut oil resin	0	0	0	0
Properties				
A. Rheometer (150°C)				
Max. torque, MPa	18.5	14.0	14.8	14.4
Min. torque, MPa	2.2	1.7	1.8	1.6
Delta torque	16.3	12.3	13.0	12.8
T ₉₀ , minutes	14.3	16.7	14.9	11.8
B. Stress-Strain				
Tensile, MPa	21.6	19.5	19.5	19.9
Elongation (%)	484	556	571	533
Modulus, 300%, MPa	11.9	8.2	7.9	9.6
C. Rebound, 100°C, %	62	60	62	63
D. Hardness, Shore A, 100°C	58	53	55	56
E. Tear Strength, N, 95°C	114	238	93	104
F. DIN abrasion	99	148	158	138

Table 14A

(a Continuation of Table 14)			
Ingredients	UU	VV	WW
Carbon black	50	35	35
Silica	0	0	0
Coupling agent	0	0	0
Starch composite	15	15	15
Hexamethoxymethylmelamine	2	2	0
Phenolic cashew nut oil resin	0	2	2
Properties			
A. Rheometer (150°C)			
Max. torque, MPa	15.2	14.4	14.5
Min. torque, MPa	2.0	2.0	1.6
Delta torque	13.2	12.4	12.8
T ₉₀ , minutes	15.9	15.6	12.2
B. Stress-Strain			
Tensile, MPa	20.4	19.5	20.5
Elongation (%)	524	550	556
Modulus, 300%, MPa	10.0	9.0	9.1
C. Rebound, 100°C, %	60	62	63
D. Hardness, Shore A, 100°C	57	54	56
E. Tear Strength, N, 95°C	116	112	111
F. DIN abrasion	141	154	139

[0170] It can readily be seen from Tables 14 and 14A that the addition of coupling agent (Sample TT), hexamethoxymethylmelamine (Sample UU) phenolic cashew nut oil resin (Sample WW) or a combination of hexamethoxymethylmelamine and phenolic cashew nut oil resin (Sample VV) improves the abrasion resistance and tear resistance of the carbon black/starch composite rubber composition (Sample SS).

[0171] It is also apparent that the addition of selected methylene donors and/or acceptors can provide higher tear resistance than the addition of coupling agent.

EXAMPLE VIII

[0172] In this Example a starch/plasticizer composite is evaluated as a filler in combination with carbon black. The addition of coupling agent to the rubber compositions which contain carbon black and starch/plasticizer composite fillers or the combination of coupling agent with methylene donor and/or methylene acceptor are compared to the Control Sample AAA.

[0173] The rubber samples were prepared using the rubber compositions shown in Table 15 in which, for the second non-productive mix stage, the coupling agent, hexamethoxymethylmelamine and phenolic cashew nut oil resin are shown as being variables. In Table 16 the variable amounts of the ingredients for the second non-productive mix stage are shown as well as various cured properties of the rubber compositions.

Table 15

Material	Parts
1st Non-Productive	
Cis 1,4-polyisoprene rubber	100
Carbon black	35
Processing oil	5
Zinc oxide	5
Antioxidant	2
Fatty acid	2
2nd Non-Productive	
Starch composite	15
Coupling agent	Variable (0 or 3)
Hexamethoxymethylmelamine	Variable (0 or 2)
Phenolic cashew nut oil resin	Variable (0 or 2)
Productive	
Sulfur	1.5
Sulfenamide accelerator	1

[0174] The Samples are vulcanized at 150°C for 36 minutes hours and various resulting physical properties are shown in Table 16.

Table 16

Ingredients	AAA	BBB	CCC	DDD	EEE
Coupling agent	0	3	3	3	3
Hexamethoxymethylmelamine	0	0	2	2	0
Phenolic cashew nut oil resin	0	0	0	2	2
Properties					
A. Rheometer (150°C)					
Max. torque, MPa	14.9	14.4	13.8	14.1	14.1
Min. torque, MPa	1.8	1.5	1.3	1.5	1.5
Delta torque	13.1	12.9	12.5	12.6	12.6
T ₉₀ , minutes	13.8	11	11.3	11.9	10.4
B. Stress-Strain					
Tensile, MPa	21.1	21.5	20.5	20.2	18.7
Elongation (%)	565	529	529	504	512
Modulus, 300%, MPa	8.7	10.5	10.2	10.8	9.5
C. Rebound, 100°C, %	66	69	67	64	61
D. Hardness, Shore A, 100°C	56	57	54	56	58
E. Tear Strength, N, 95°C	95	103	121	135	137
F. DIN abrasion	158	151	162	154	143

[0175] It can be seen from Table 16 that the addition of coupling agent to the starch/plasticizer composite (Sample BBB) is observed to improve the tear strength and abrasion resistance of the control rubber compound (Sample AAA). The addition of the coupling agent and specified methylene donors and/or acceptors (Samples CCC, DDD and EEE) is observed to provide a further improvement in tear resistance as compared to Sample BBB.

Claims

1. A rubber composition characterized by comprising (A) 100 parts by weight of at least one diene-based elastomer, (B) 0.1 to 120 phr of at least one elastomer reinforcing filler composed of (1) from 0.1 to 120 phr of at least one starch-based material selected from at least one of starch, starch/ plasticizer composite and modified starch, wherein said modified starch is selected from at least one of hydroxyethylated starch, oxidized starch and acid modified starch, and (2) zero to 90 phr of (a) carbon black and amorphous silica, or (b) carbon black or amorphous silica, (C) optionally a coupling agent for said starch-based material and silica, if silica is used, where said coupler has a moiety reactive with the surface of said starch composite and the surface of said silica, as the case may be, and a moiety interactive with the said elastomer, and (D) at least one methylene acceptor compound and/or methylene donor compound exclusive of hexamethylene tetramine.
2. The rubber composition of claim 1 characterized in that said rubber composition contains a methylene acceptor compound selected from at least one of phenolic cashew nut oil resin, resorcinol monobenzoate and polyhydric phenoxy resin and/or a methylene donor compound selected from at least one of hexamethoxymethylmelamine, hexaethoxymethylmelamine and ethoxymethylpyridinium chloride, N,N',N''-trimethylolmelamine, N-methylolmelamine and N',N''-dimethylolmelamine.
3. The rubber composition of any of the preceding claims characterized in that said starch based material is starch composed of amylose units and amylopectin units in a ratio of 15/85 to 35/65 and has a softening point according to ASTM No. D1228 in a range of 180°C to 220°C.
4. The rubber composition of any of the preceding claims 1 and 2 characterized in that said starch based material is corn starch.
5. The rubber composition of any of the preceding claims 1, 2 and 4 characterized in that said starch based material is a starch/plasticizer composite wherein said starch/plasticizer composite has a softening point in a range of 110°C to 170°C according to ASTM No. D1228, said plasticizer is a polymeric plasticizer having a softening point of less than 160°C selected from at least one of comprised of at least one of poly(ethylenevinyl alcohol), ethylene-vinyl acetate copolymers, ethylene-glycidal acrylate copolymers and ethylene-maleic anhydride copolymers, ethylene-vinyl alcohol copolymers, and ethylene-acetate vinyl alcohol terpolymers so long as they have a softening point lower than 160°C and lower than the softening point of the starch and wherein the weight ratio of starch to plasticizer is in a range of 0.5/1 to 4/1.
6. The rubber composition of any of the preceding claims 1 and 2 characterized in that said starch based material is a modified starch selected from at least one of hydroxyethylated starch and oxidized starch wherein, for said hydroxyethylated starch, hydroxyethyl groups have been substituted for a minor portion of hydroxyl groups of the starch.
7. The rubber composition of any of the preceding claims characterized by containing from 20 to 85 phr of reinforcing filler selected from at least one of carbon black and amorphous silica.
8. The rubber composition of any of the preceding claims characterized in that a coupling agent is used and wherein said coupling agent is comprised of a bis (3-trialkoxysilylalkyl) polysulfide wherein said alkyl groups for the trialkoxy component are selected from methyl and ethyl radicals, wherein said alkyl group for said silylalkyl component is selected from ethyl, propyl and butyl radicals and wherein the polysulfide bridge contains an average of 2.2 to 4 connecting sulfur atoms.
9. A rubber composition of claim 1 characterized by comprising (A) 100 parts by weight of at least one diene-based elastomer selected from at least one polymer or copolymer of isoprene and/or 1,3-butadiene and copolymer of at least one of isoprene and 1,3-butadiene with styrene, (B) 25 to 90 phr of at least one elastomer reinforcing filler composed of (1) 5 to 70 phr of at least one starch-based material selected from at least one of starch, starch/plasticizer composite having a Tg in a range of 110°C to 170°C and modified starch, wherein said modified starch is

selected from at least one of hydroxyethylated starch, oxidized starch and acid modified starch, and (2) 20 to 85 phr of carbon black and/or amorphous silica (C) a coupling agent for said starch-based material and silica where said coupler has a moiety reactive with the surface of said starch composite and the surface of said silica and a moiety interactive with the said elastomer, and (D) at least one methylene acceptor compound and/or methylene donor compound exclusive of hexamethylene tetramine; wherein said methylene acceptor is a phenolic cashew nut oil resin and said methylene donor is selected from at least one of hexamethoxymethylmelamine, hexaethoxymethylmelamine and ethoxymethylpyridinium chloride, N,N',N"-trimethylolmelamine, N-methylolmelamine and N',N"-dimethylolmelamine and wherein said coupling agent is comprised of a bis (3-trialkoxysilylalkyl) polysulfide wherein said alkyl groups for the trialkoxy component are selected from methyl and ethyl radicals, wherein said alkyl group for said silylalkyl component is selected from ethyl, propyl and butyl radicals and wherein the polysulfide bridge contains an average of 2.2 to 4 connecting sulfur atoms.

10. A tire characterized by having at least one component comprised of the rubber composition of any of the preceding claims.



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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 6142

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 3 480 572 A (RUSSELL CHARLES R ET AL) 25 November 1969 (1969-11-25) * abstract * * column 1, line 36 - line 55 * * column 2, line 62 - line 72 * * example 4 * * claim 1 * ---	1,2	C08L21/00 C08L9/00 C08K5/17 B60C1/00
X	US 4 942 192 A (YASUDA TAKUO ET AL) 17 July 1990 (1990-07-17) * abstract * * column 2, line 18 - line 49 * * column 3, line 14 - line 16 * * column 3, line 41 - line 46 * * column 4, line 25 - line 37 * * column 5, line 7 - line 23 * * examples 1-11 * * claims 1-5 * ---	1,2	
E	EP 1 038 697 A (GOODYEAR TIRE & RUBBER) 27 September 2000 (2000-09-27) * abstract * * page 3, line 13 - line 31 * * page 1, line 41 - line 44 * * page 3, line 56 - line 58 * * page 4, line 6 - line 41 * * table 1 * * claims 1-3 * ---	1-5,7,8, 10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08L C08K C08J B60C
A	EP 0 795 581 A (GOODYEAR TIRE & RUBBER) 17 September 1997 (1997-09-17) * abstract * * page 3, line 32 - line 42 * * page 3, line 52 - page 4, line 20 * * page 4, line 42 - line 46 * * page 6, line 32 - line 42 * * claims 1-4,11 * --- -/--	1-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 December 2000	Examiner Denis, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P04C01)



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EUROPEAN SEARCH REPORT

Application Number
EP 00 11 6142

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 December 2000	Examiner Denis, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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